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DEPARTMENT OF RESEARCH TECHNOLOGY PLANTING.ADVERTISINGTHE USE OF SUPPERON IN QUALITATIVE CHEMICAL ANALYSIS.

By

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1. Use of supperon in micro-analysis

One of the interesting series of uranium minerals is formed by the uranium micas. Considered chemically, the uranium micas are tri-substitution double hydrous salts of the divalent group RO (Ca, Cu, Ba, Mg, Pb, K₂, Na₂) and uranyl -O₂ of orthophosphoric, orthoarsenic and vanadic acids or tri-substituted hydrous salts of uranyl. The most characteristic of the extensive group of micas found in U.S.S.R. are tyuyamunite - $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$, which owes its name to the locality where it is found, Tyuya-Muyun in Central Asia; torbenite - $\text{CuO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$, found at Taboshar in Bolek; zimmerite of the same locality with the formula: $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ and others.

The lack of simple, rapid methods of analysis and sensitive reactions for uranium considerably increases the laboratory analysis of the corresponding ores and complicates the assessment of uranium in geological field surveys.

The reactions for the detection of uranium in the form of uranyl sodium acetate, tri-acetate⁽¹⁾ or in the form of thallium uranyl carbonate⁽²⁾, as recommended in recent textbooks on microchemical analysis, are somewhat complicated and are not always successful, even when pure reagents are employed. They are still more difficult in the detection of uranium in natural ores. The importance of microchemical techniques in geological and mineralogical work is continually increasing. In certain cases, it is only possible by microchemical methods to carry out the necessary determinations at all. V.G. Melkov and S.G. Surikov⁽³⁾ have shown that "microchemical analysis is the only method which ensures the possibility of detecting micas of different chemical

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compositions". At another place, they write⁽³⁾: "The small quantities in which uranium micas occur in nature, their optical close relationship and their resemblance in colour and other physical properties induced us, as far back as in 1936, to consider and recommend the microchemical method of identifying such minerals as one of the most effective".

The foregoing, together with the necessity of making frequent determinations of uranium in micas (the subject of our work is the investigation of the properties of uranium micas) caused us to make a search for a more sensitive, simple and rapid reaction for uranium.

In some of our earlier investigations⁽⁵⁾ it was found that cupferron is a very sensitive reagent for many cations (Li^+ , Ba^{++} , Ca^{++} , Sr^{++} , In^{++} , Bi^{++} , Cd^{++} , Hg^{++}) and may be used in qualitative micro-analysis. The present investigation forms a continuation of the previous work with a view to extending the field of application of cupferron to the qualitative analysis of uranium, vanadium and iron.

The detection of uranium is carried out as follows:

A drop of the solution to be tested is placed on an object glass and alongside it is placed a drop of a 6% solution of cupferron. The drops are caused to unite by means of a glass rod. There forms at once an amorphous precipitate, from which crystals of uranyl-nitrosophenylhydroxylamine gradually appear.

The crystals dissolve in concentrated hydrochloric acid, sulphuric acid and nitric acid.

Sensitivity of the reaction: 0.006 milligrams of uranium per millilitre of solution.

It should be observed that vanadium gives a dark red precipitate with cupferron. If vanadium is present simultaneously with uranium, it masks the formation of crystals of uranyl-nitrosophenylhydroxylamine.

The proposed reaction was tried out on the natural minerals: uraninite - $(\text{UTh})\text{O}_2$, $\text{UO}_3 \cdot \text{PbO}$, tynnanite - $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and uranium mica of the constitution $\text{CuO} \cdot \text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ and gave good results. For the detection of
/uranium,

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uranium, a small piece of the natural mineral was ground to a fine powder and dissolved in dilute sulphuric acid with gentle warming. The solution was filtered from suspended matter, and the uranium was detected in the filtrate by placing a drop of the test solution on an object glass and adding a drop of cupferron solution to it. In tyuyamunite, after the addition of cupferron, crystals of $\text{Ca}(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_2$, previously described by us, are precipitated at first, followed by small crystals of uranyl-nitrosophenylhydroxylamine.

II. Use of cupferron in drop tests

(a) Detection of vanadium. For the detection of vanadium by drop test, use is made of the reaction of the oxidation of aniline by vanadic acid in an acid medium. (4) Concentrated hydrochloric acid is used for acidification. Vanadium may be detected with equal success in a drop test by the reaction with cupferron, without the use of concentrated acid. A drop of a solution of vanadate is placed on a piece of filter paper and when it has been absorbed by the paper, a drop of cupferron is placed on it. An intense blood red colour is immediately produced. Fe^{++} and Fe^{+++} , which give a red colour with cupferron, interfere with the detection of vanadium.

Sensitivity of the reaction: 0.0002 milligram per millilitre of solution. The effectiveness of the colouring and the sensitivity of the test are enhanced by placing a drop of cupferron first on the glass and then a drop of the solution to be tested.

A drop of ammonia placed on the coloured spot causes the colour to disappear but it re-appears on the addition of a drop of nitric acid.

(b) Detection of iron. If a drop of cupferron is placed on a filter paper and a drop of iron salt is superposed on it, a red colour with a yellow tinge is formed in the case of Fe^{+++} and a red colour in the case of Fe^{++} . With low concentrations of iron, the colour is yellow.

The sensitivity of the reaction is such that it is possible to detect iron up to 0.0002 milligrams per millilitre of solution.

III. Detection of vanadium and iron in test tube analysis

With salts of vanadic acid, NH_4VO_3 , NaVO_3 etc. cupferron gives a thick
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blood red precipitate. On the addition of ammonia or alkali solution to the precipitate, the solution loses its colour and the precipitate is dissolved. The addition of nitric acid restores the red colour of the solution.

The test is extremely sensitive. It was stated above that in the action of cupferron on Fe^{++} and Fe^{+++} the reaction is externally analogous to that with vanadium. In this connection, when vanadium and iron are present together, the precipitate, after the addition of cupferron, is dissolved in ammonia and the solution filtered. Iron in the form of hydroxide remains on the filter and the vanadium compound is in the filtrate. The iron is detected in the usual way and the vanadium is detected in the filtrate by the action of nitric acid (the solution is coloured red).

Conclusions

1. In its simplicity, sensitivity and rapidity, the reaction of cupferron on uranium may be successfully used in micro-analysis for the detection of uranium not only when working with pure reagents but for the analysis of natural minerals and ores.
2. In drop tests and test-tube tests, the reaction with cupferron may be used for the detection of vanadium and iron.

References

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